

Researches on Explosives. Part IV.

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[PLATE 6.]

(Abstract.)

In Part III of my "Researches on Explosives," I gave the results of a very extensive series of experiments, the completion of which necessarily occupied a very long time, and the particular explosives with which I experimented were those with which artillerists in this country were familiar, and with which a considerable number of experiments had been made.

These explosives were, first, the cordite of the Service, known as Mark I second, the modified cordite, known as M.D.; and third, the nitrocellulose, known as Rottweil R.R. The experiments made by myself extended, for all the above explosives, from densities of 0·05 to 0·45 or 0·50, and pressures of from 2·75 tons per square inch (419 atmospheres) to pressures of 60 tons per square inch (9145 atmospheres).

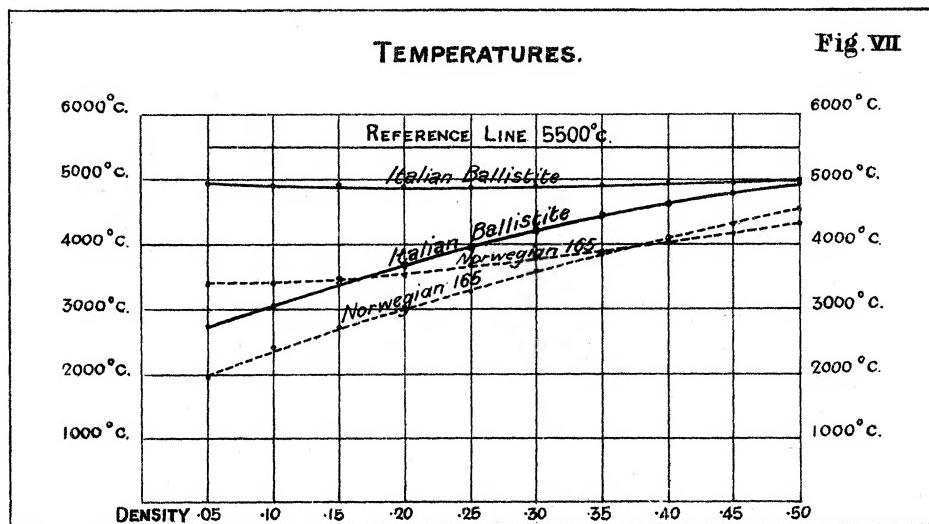
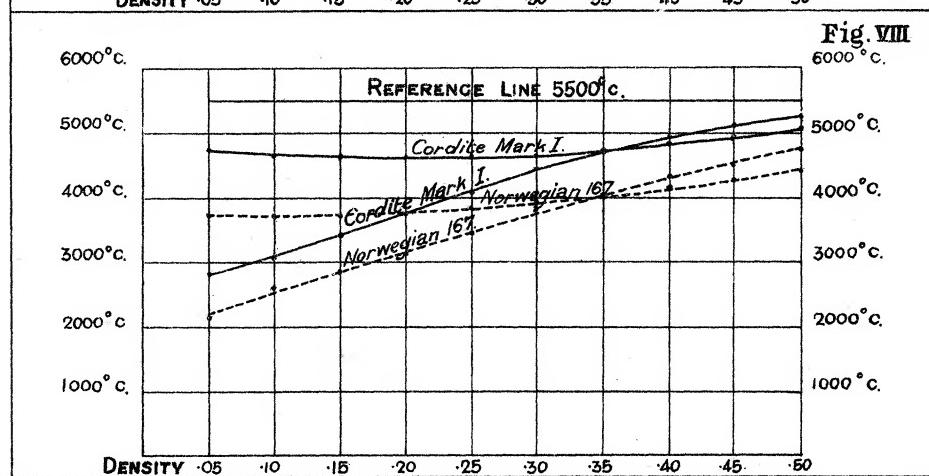
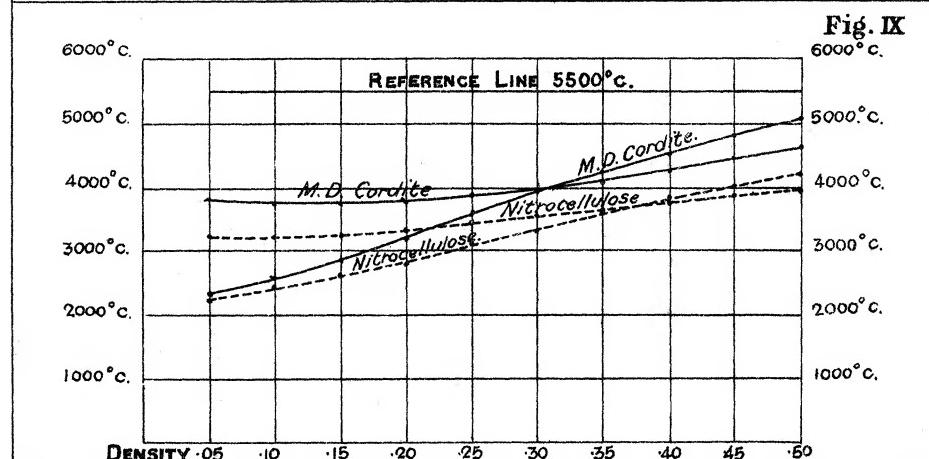
The composition of the various explosives referred to are given, and experiments quoted to show that the transformation experienced on explosion at different densities is practically identical.

When explosives are fired in a gun, the chamber in which the charge is placed is, of course, full of air, and in my experiments the charges were similarly treated, but, to test the resulting differences, charges were fired at the lowest densities in air, in nitrogen, and *in vacuo*, and the analyses of the products of explosion are given, and compared with the analyses of gases taken from the chamber of a gun after discharge.

Although for the elucidation of the laws which govern the transformation of the explosives when fired I have taken the densities named, I must point out that the requirements of the artillerist are confined to much narrower limits, the density, of course, varying considerably with the particular explosive used.

In modern guns, for example, the chamber density varies from about 0·310 to nearly 0·500, a good deal of the variation being due to the nature of the explosive used. It is hardly necessary to point out to artillerists that the chamber density is not the density which is responsible for the pressure developed in the gun.

The difference, which is frequently very considerable, is due to the time

**Fig. VII****Fig. VIII****Fig. IX**

taken by the explosive to burn, and this depends upon the nature, form, and dimensions of the explosive, the expansion suffered by the nascent gases, and the heat lost, due to work done upon the projectile and by communication of heat to the gun, and, under these circumstances, the pressure developed would, with full charges, if compared with close-vessel pressures, represent densities approximately between 0·17 and 0·23.

The tables which are given in my late communication* to the Royal Society gave for each particular density the actual result observed. In the present paper the observations have been corrected by drawing curves to represent as nearly as possible the whole of the results, the actual observations, which are also given, showing in each case the departure from the curve. If reference be made to the tables,† it will be observed how wide are the differences between the explosives, not only in the absolute volumes of the several gases, but in the variations with reference to the densities at which they were fired.

Thus, for example, comparing Norwegian 165 and Italian Ballistites, while in the former the carbon monoxide commences at the density 0·05 with a percentage volume of 38·5, falling at a density of 0·45 to 22 per cent., the carbon dioxide commences with 13·3 per cent., rising rapidly to 31 per cent. In the latter explosive the CO commences at 20·5 per cent., and falls slowly to 15 per cent., while the CO₂ commences a little over 26 per cent., rising also comparatively slowly to nearly 34 per cent.

I may remark in passing that the Italian Ballistite is the only explosive with which I have experimented where, at low densities, the volume of CO₂ is greater than that of CO.

But there are, in these two explosives, other remarkable differences. Thus, in the Italian Ballistite, at a density of 0·05, the volume of methane, CH₄, is a mere trace, about 0·02 per cent., but it remains very much lower than is the case with any other explosive, being only 1·9 per cent. at the density of 0·45. With the Norwegian, on the other hand, the CH₄, although the volume at commencement is only 0·04 per cent., is, at 0·45 density, 11 per cent.

Again, as might be expected from the large quantity of CH₄ found in the case of the Norwegian Ballistite, the volume of hydrogen falls from over 20 per cent. to about 9 per cent.; in the Italian the H rises from about 8 per cent. to about 10 per cent., falling slightly at higher densities.

In both explosives the N is practically constant at about 12 and 16 per cent. respectively, but there is a very great difference as regards the

* 'Phil. Trans.', vol. 205, pp. 221—223.

† Not given in this abstract.

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H_2O . In the Norwegian the H_2O is constant at 14 per cent., there being no greater difference than might be expected from errors of observation, while in the Italian the H_2O , which commences at density 0·05 with a volume of 29 per cent., falls at a density of 0·45 to about 24 per cent. No other explosive approaches the Italian Ballistite in respect to the large volume of aqueous vapour formed, especially at low densities.

In the tables are given the volumes in cubic centimetres per gramme of the permanent and total gases, and curves have been drawn representing for the six explosives the observations of these volumes. In the case of five of the explosives there is, with increasing density, a very considerable decrease in volume, but with the Italian Ballistite, throughout the range of the experiments, there is hardly any change. Curves representing these volumes are concave to the axis of abscissæ.

In the tables are shown the units of heat, both for water fluid and water gaseous. Curves have also been drawn for the units of heat (water gaseous); the curves in this instance are all convex to the axis of abscissæ, and it may be noted that, where the volumes of gas per gramme are large, the units of heat are low, and that, where the volumes of gas are rapidly decreasing, the curves representing the amount of heat developed show a rapid increase.

The next point we have to consider is, the data being as shown in tables, what temperature are we to assign to that generated by the explosion? With the view of studying the question, I resorted to two methods: (1) knowing with very considerable accuracy the units of heat (water gaseous) generated by the explosion, and having determined approximately the specific heat of the gases, the temperature of explosion should be given by the equation

$$t = \frac{\text{gramme units of heat}}{\text{specific heat}} \quad (1)$$

(2) Knowing also with considerable accuracy the pressure at any given density, and knowing the pressure p_0 when the volume of gas generated is reduced to the temperature of 0° C. and a pressure of 760 mm. of mercury, the temperature is given by the equation

$$t = \frac{p - p_0}{0.00367 \cdot p_0} \quad (2)$$

With reference to Equation (1), the specific heat of CO_2 is a very important factor in this determination, and the recent researches of Messrs. Holborn and Austin upon the specific heat of gases at constant pressure at high temperatures having apparently shown that the specific heats given by Mallard and Le Chatelier for temperatures above 100° C. are considerably too high, I have taken the figures given by these physicists—which, I may observe, up to temperatures of 800° C. are confirmed by Langen.

The equation given by Holborn and Austin for the specific heat of CO₂ at constant pressure is

$$\text{Specific heat} = 0.2028 + 0.000,128,4\theta - 0.000,000,05 \theta^2,$$

θ being the temperature.

The correctness of this equation for temperatures up to 800° C. has been proved, and, assuming that the same equation holds up to 1300° C., the specific heats for each 100° are given in a table in the full paper.

It will be observed from this table, that, although between 0° and 1400° C. there is a large increase in the value of the specific heat, yet the increments per 100° are rapidly decreasing, vanishing altogether at about 1400° C., at which temperature* there would be partial dissociation at atmospheric pressure. The temperature would, however, probably require to be considerably higher at the pressures we are considering.

The specific heats given are, as I have said, those for constant pressure, and to obtain those at constant volume it is necessary to divide by the constant k , connecting the specific heats of gases and vapours at constant pressure and constant volume.

I give the values I have used, (1) of the specific heats at constant pressure—these are taken either from Holborn and Austin's paper, or from Landolt Börnstein, 'Physikalisch-Chemische Tabellen,' 1905; (2) of the constant k —these are all taken from Landolt, pages 407–8; (3) of the specific heats at constant volume.

Gases, etc.	Specific heat, constant pressure.	Value of k .	Specific heat, constant volume.
CO ₂	0.2986	1.282	0.232
CO	0.2425	1.401	0.173
H	3.4100	1.408	2.422
CH ₄	0.5922	1.316	0.450
N	0.2497	1.410	0.177
H ₂ O	0.4210	1.330	0.361

The specific heats calculated from the above data, of the gases generated by the explosion of the six propellants, are given in the tables embodying the results of the whole of the experiments for each propellant, and in the tables are also given the temperatures of explosion deduced from Equations (1) and (2), and here again it must be remembered that the temperatures with

* Mendeleef, 'Principles of Chemistry,' vol. 1, p. 381; also Deville, 'Comptes Rendus,' vol. 56, p. 729; and Berthelot, 'Comptes Rendus,' vol. 68, p. 1035.

which artillerists are chiefly concerned are those due to densities varying approximately between 0·17 and 0·23.

Beginning with Equation (1), the Italian Ballistite, which shows the highest temperature, commences at the density of 0·05 with 4943° C., this temperature hardly varying at all till the density of 0·25 is reached, when it slowly but regularly increases to about 5000° C. at $d=0\cdot45$. Cordite Mark I commencing at 4742° C. with a very slight fall is practically constant up to $d = 0\cdot30$, after which it rises somewhat rapidly to a temperature of 4921° C. at $d = 0\cdot45$, and to 5065° C. at $d = 0\cdot50$.

When, however, we come to the temperatures given by Equation (2), we are met with some very remarkable differences, which are shown by the tables, but which are more readily appreciated if reference be made to reduced copies of Plates 7, 8, and 9, in which the explosives are arranged in descending order of the temperatures developed.

It will be observed that at the higher densities and pressures, there is generally a very tolerable accordance in the temperatures obtained from the two formulæ, but as the density and pressure diminish, the divergence becomes in all cases considerable, but very greatly more with the explosives which develop very high temperatures, and which give rise to large percentages of carbonic anhydride.

The only construction I am able to put upon the tolerably close approximation of temperature given by the two formulæ at high densities and pressures, and the wide differences which exist in some of the explosives at low densities, is that, as I think it reasonable to expect, at high densities dissociation of the carbonic anhydride is prevented by the very high pressure, and that the great difference between, for instance, Italian Ballistite and Nitrocellulose R.R. at, say, the density of 0·1 is due, firstly, to the difference of the temperature at which the nascent gases are generated, and secondly, to the proportion of CO₂ which is subject to dissociation.

Formula (1) gives for Italian Ballistite at $d = 0\cdot1$ a temperature of nearly 5000° C. (and for this explosive the temperature given by units of heat divided by specific heat is nearly constant), while the percentage of CO₂ is 38·2. The same formula gives for the nitrocellulose at the same density a temperature of formation of 3200° C., while the percentage of CO₂ is only 19·45.

I have pointed out that under atmospheric pressure the dissociation of CO₂ commences at about 1300° C., and the very much higher temperatures of formation of the gases of the Italian Ballistite, combined with its double percentage of CO₂, appear to me to be sufficient to explain the results obtained with this explosive.

If reference be made to fig. VII on Plate 6, it will be seen that while at the

density of 0·1 there is, with Italian Ballistite, a difference of about 1800° C. between the two formulæ, there is with the nitrocellulose a difference only of under 800° C.

The theory I venture to submit is as follows :—

The nascent gases are generated at temperatures approximately as given by Equation (1) and by the upper curve of each explosive in figs. VII, VIII, and IX.

Under the low densities and pressures at the very high temperatures with which we are concerned, the CO₂, and possibly some H₂O, are partially dissociated, giving rise to the fall in temperature exhibited by the results obtained from Equation (2).at low densities. At high densities, as already pointed out, the two equations give, in some cases, accordant results, in all cases tolerable agreement ; it therefore appears to me to be reasonable to suppose that the facts I have recorded are due to partial dissociation at low densities and pressures, which dissociation is prevented by the very high pressures ruling at densities of 0·40, 0·45, and 0·50.

As no free oxygen is ever found in the analyses, in cooling down, any free oxygen due to dissociation must have re-combined, and the heat lost by dissociation regained. The re-combination must, however, be very gradual, as no discontinuity is observed in the cooling curves.

It is then pointed out that a certain amount of confirmation is given to the view taken by the fact that if the explosives be arranged according to the amount of heat generated, derived from Equation (1), regard being also had to the amount of CO₂ found, it will be found that the differences between the two formulæ decrease approximately as the factors, to which I have referred, decrease, and a table is given showing these differences.

At the density of 0·45 the differences between the two formulæ are as follows :—

	Difference.
Italian Ballistite.....	150° C.
Cordite Mark I	200
M.D.....	320
Norwegian Ballistite 167	250
Norwegian Ballistite 165	130
Nitrocellulose	180

It will be observed, both from the above figures and the curves, that with the Italian Ballistite alone at the density 0·45 is the temperature derived from Equation (2) lower than that derived from Equation (1). With all the other explosives the temperatures derived from Equation (2) are the higher.

The differences, however, are not great, being generally under 5 per cent., that is, under 200° C.

In the case of experiments carried on both at pressures and temperatures very greatly above the limits at which physicists ordinarily experiment, I can hardly hope that the methods I have employed, and the conclusions at which I have arrived, will escape criticism.

The results of the experiments given in the tables and plates, may, however, be taken as very approximately correct, and the repeat experiments I have made show that there is great constancy in the transformation which takes place on explosion at any given density.

I conclude by expressing my obligation to Dr. Sodeau and Mr. Hutchinson for their assistance in carrying out the various experiments, in the analyses and in the laborious but necessary calculations.

Note.—In the case of the Norwegian Ballistites, the pressures at densities above 0·3 have been corrected to accord with the values obtained from the volume of the gas generated, multiplied by the units of heat determined.
